

Allenes. Part XI.* The Preparation of 3-Alkyl- and 3,3-Dialkyl-1-bromoallenes

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3-Alkyl- and 3,3-dialkyl-1-bromoallenes are prepared in excellent yield by the action of hydrobromic acid (45—50%) on secondary or tertiary acetylenic carbinols. They show an exceptionally intense band in the infrared region, a small maximum in the ultraviolet region above 210 $m\mu$, and the expected n.m.r. long range spin-spin coupling.

1-BROMOALLENES are useful starting materials for the synthesis of compounds containing the allene group.^{1,2} We now describe methods developed in our laboratories for the preparation of 1-bromoallenes.³

Early reports in the literature⁴ suggested that the action of concentrated hydrobromic acid on the tertiary acetylenic alcohol 3-methylbut-1-yn-3-ol gives 1-bromo-3-methylbuta-1,3-diene and not the allene. Moulin⁵ also reported that dry hydrogen bromide reacted with the same alcohol to give 1,3-dibromo-3-methylbutene and 1,2,3-tribromo-3-methylbutane.

In our hands 1-bromoallenes were always obtained in good yield from acetylenic alcohols and concentrated hydrobromic acid unless the reagents were subjected to prolonged and excessive heating, *i.e.*, to temperatures $>40^\circ$. Initially no catalyst was used, but it soon became apparent that, although 1-bromoallenes were obtained after shaking the reaction mixture for 1—3 weeks, the reaction did not go to completion even after these prolonged periods. Although mechanistically interesting, the procedure is preparatively unattractive.

(a) Tertiary alcohols of low molecular weight are treated with 2.2 moles of 45—48% hydrobromic acid, 0.35 mole of cuprous bromide, 0.34 mole of ammonium bromide, and 0.035 mole of copper powder per mole of alcohol for 1—2 hr. at 35—40°, or 8—12 hr. at room temperature.

(b) Tertiary alcohols of high molecular weight, and sterically hindered alcohols, are agitated with 3.2 moles of 45—48% of acid, 1 mole of cuprous bromide, 1 mole of ammonium bromide, and 0.1 mole of copper powder per mole of alcohol at 35—40° for 2—20 hr.

(c) Secondary alcohols are treated with 2.2 moles of 60% hydrobromic acid, 1 mole of cuprous bromide, 1 mole of ammonium bromide, and 0.1 mole of copper powder at room temperature for 20—30 hr.

Pure dialkyl-1-bromoallenes are obtained from tertiary acetylenic alcohols, but mono-alkyl-1-bromoallenes may contain up to 5% of the isomeric 3-bromoacetylenes, which may be separated by careful fractionation. Most 1-bromoallenes are reasonably stable and may be stored at low temperature for long periods;

TABLE I

The infrared spectra of 1-halogenoallenes *

ϵ_a^v = apparent extinction coeff. at wavenumber ν in l. mole ⁻¹ cm. ⁻¹ .	$\Delta\nu_{\frac{1}{2}}^a$ = corresponding half-band width in cm. ⁻¹
1-Chlorohexa-1,2-diene ^a	$\epsilon_a^{1965} = 12.8$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{840} = 23.2$ $\Delta\nu_{\frac{1}{2}}^a = 20$ $\epsilon_a^{745} = 111$ $\Delta\nu_{\frac{1}{2}}^a = 12$
1-Bromohexa-1,2-diene	$\epsilon_a^{1970} = 23.2$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{880} = 30.9$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{745} = 19.3$ $\Delta\nu_{\frac{1}{2}}^a = 12$
1-Iodobexa-1,2-diene ^b	$\epsilon_a^{1950} = 12.5$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{880} = 33.3$ $\Delta\nu_{\frac{1}{2}}^a = 10$
1-Chloro-3,4,4-trimethylpenta-1,2-diene ^c	$\epsilon_a^{1955} = 40.5$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{880} = 23.5$ $\Delta\nu_{\frac{1}{2}}^a = 8$ $\epsilon_a^{740} = 152$ $\Delta\nu_{\frac{1}{2}}^a = 20$
1-Bromo-3,4,4-trimethylpenta-1,2-diene	$\epsilon_a^{1955} = 47.3$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{880} = 24.6$ $\Delta\nu_{\frac{1}{2}}^a = 8$ $\epsilon_a^{730} = 133$ $\Delta\nu_{\frac{1}{2}}^a = 12$
1-Bromo-3-methylpenta-1,2-diene	$\epsilon_a^{1975} = 57.1$ $\Delta\nu_{\frac{1}{2}}^a = 15$
1-Iodobuta-1,2-diene ^b	$\epsilon_a^{1950} = 12.6$ $\Delta\nu_{\frac{1}{2}}^a = 15$ $\epsilon_a^{880} = 105$ $\Delta\nu_{\frac{1}{2}}^a = 15$ †

* 10% solution in liquid paraffin, 0.1 mm. cell. † Also $\epsilon_a^{880} = 32.4$, $\Delta\nu_{\frac{1}{2}}^a = 8$.

^a T. L. Jacobs, W. L. Petty, and E. G. Teach, *J. Amer. Chem. Soc.*, 1960, **82**, 4094. ^b C. S. L. Baker, P. D. Landor, S. R. Landor, and A. N. Patel, *J. Chem. Soc.*, 1965, 4348. ^c Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 1959, 24; R. D. J. Evans and S. R. Landor, *ibid.*, 1965, 2553.

The presence of equivalent quantities of cuprous bromide and ammonium bromide effects a dramatic increase in the speed of the reaction, which is readily followed, as two layers are rapidly formed and the mixture is agitated until infrared (i.r.) examination of small samples of the upper layer does not show a hydroxyl band (3500 cm^{-1}).

Bromoallenes are best prepared from aliphatic alcohols as follows.

* Part X, D. K. Black and S. R. Landor, *J. Chem. Soc.*, 1965, 6784.

¹ C. S. L. Baker, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 1965, 4659.

² P. M. Greaves, S. R. Landor, and D. R. J. Laws, *Chem. Comm.*, 1965, 321.

1-bromo-3-methylbuta-1,2-diene is the least stable of the simple 1-bromoallenes, and tends to isomerise to 1-bromo-3-methylbuta-1,3-diene and polymerise; this may account for the early results by the Russian workers in which bromoallenes were not obtained.

1-Bromoallenes were found to possess unusual spectroscopic properties. The 1950 cm^{-1} allenic C=C stretching band in the i.r. region is exceptionally intense compared with those of 1-chloro- and 1-iodo-allenes (Table 1);

³ For a preliminary account see D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, 1963, 483.

⁴ T. A. Favorskaya, *Zhur. obshchei Khim.*, 1940, **10**, 461; T. N. Nazarov and Ya. N. Yanbikov, *Bull. Acad. Sci. U.R.S.S. Class. Sci. chem.*, 1941, 566.

⁵ Fr. Moulin, *Helv. Chim. Acta*, 1951, **34**, 2416.

3,3-dialkylbromoallenes show strong bands near 1165 and 725 cm^{-1} , possibly the C^1H in-plane and out-of-plane deformation bands. Both bands decrease in intensity on partial deuteration of C^1 , showing them to be CH vibrations, and a new band δ appears at 870 cm^{-1} .

Pure 1-halogenoallenes show a maximum in the ultraviolet (u.v.) region at 200–206 $\text{m}\mu$. Monoalkylbromoallenes also show an inflection at 215 $\text{m}\mu$, and dialkylbromoallenes a shoulder or a maximum at 217–227 $\text{m}\mu$. The intensity of this 215–227 $\text{m}\mu$ band increases markedly with increasing substitution. Chloroallenes show no maximum above 205 $\text{m}\mu$, but iodoallenes have a small maximum at 239 $\text{m}\mu$ (Table 2). There is no obvious explanation of these properties, but it is possible that they arise from a nonbonded interaction of the bromine with the π bonds of the allene system.

TABLE 2
Ultraviolet absorptions

	$\lambda_{\text{max.}}(\text{m}\mu)$	ϵ	$\lambda_{\text{max.}}(\text{m}\mu)$	ϵ
1-Chlorohexa-1,2-diene	204	3300		
1-Bromohexa-1,2-diene	205	8000	217sh	5800
1-Iodohexa-1,2-diene	207	12,000	239	4000
1-Bromo-3-methylpenta-1,2-diene	201	7100	217–223	6150
1-Bromo-3,4,4-trimethylpenta-1,2-diene	201	9000	224	6600
1-Bromo-3-t-butyl-4,4-dimethylpenta-1,2-diene ...	201	12,100	227	7400

The nuclear magnetic resonance (n.m.r.) spectra are in good agreement with those of Snyder and Roberts ⁷ for 1-chlorobuta-1,2-diene and 1-chloro-3-methylbuta-1,2-diene (Table 3).

TABLE 3
N.m.r. results

Compounds	τ Values	Spin-spin coupling constants in c./sec.
$\text{Br}-\text{CH}=\text{C}=\text{CH}-\text{Me}$ 1 2 3 4	τ_1 4.09 τ_3 4.68 τ_4 8.22	$J_{1,3}$ 5.8 $J_{3,4}$ 6.9 $J_{1,4}$ 2.6
$\text{Br}-\text{CH}=\text{C}(\text{Me})=\text{C}-\text{CH}_2-\text{Me}$ 1 2 3 4 5	τ_1 4.1 τ_4 7.4–8.6 τ_5 8.93	$J_{1,4}$ 2.3 $J_{1,5}$ 2.0 $J_{4,5}$ 0.5 $J_{4,5}$ 7.5
$\text{Br}-\text{CH}=\text{C}(\text{Et})=\text{C}-\text{CH}_2-\text{Me}$ 1 2 3 4 5	τ_1 4.0 τ_4 7.85 τ_5 8.94	$J_{1,4}$ 2.2 $J_{4,5}$ 7.6
$\text{Br}-\text{CH}=\text{C}(\text{Bu}^t)=\text{C}-\text{Me}$ 1 2 3 4	τ_1 4.17 τ_4 8.21	$J_{1,4}$ 2.0
$\text{Br}-\text{CH}=\text{C}(\text{Bu}^t)_2$ 1	τ_1 4.16	

EXPERIMENTAL

Light petroleum had b. p. 40–60°; gas-liquid chromatography (g.l.c.) was carried out with nitrogen flow rate 2 l./hr. unless otherwise stated; i.r. spectra were determined on liquid films (in a 0.025 mm. cell) and on 5% solutions in chloroform with a Perkin-Elmer Infracord spectrometer; u.v. spectra on ethanolic solutions with a Bausch and Lomb Spectronic 505 spectrometer; n.m.r. spectra with A.E.I. and Perkin-Elmer 60 Mc./sec. spectrometers for 20% solutions in carbon tetrachloride, with tetramethylsilane as

internal standard. The progress of the reactions was followed by removing small samples from the upper layer for i.r. examination, and continuing the reaction until $\nu_{\text{max.}}$ 3400–3500 cm^{-1} (OH) had disappeared.

1-Bromo-3-methylbuta-1,2-diene.—(a) 3-Methylbut-1-yn-3-ol (67.2 g., 0.8 mole) was added to a mixture of powdered cuprous bromide (40 g., 0.28 mole), powdered ammonium bromide (32 g.), copper powder (2 g.), and hydrobromic acid (48% w/w, sp. gr. = 1.5, 192 ml., 1.7 mole). The stirred mixture was warmed to 30° for 1 hr. The upper layer then showed no $\nu_{\text{max.}}$ 3400 cm^{-1} (OH). The mixture was cooled, filtered, the residue washed with light petroleum, the filtrate separated, and washed with 48% hydrobromic acid until the lower layer shows no violet coloration. The upper layer was dried (NaHCO_3 , MgSO_4) and fractionated, giving 1-bromo-3-methylbuta-1,2-diene (90 g., 77%), b. p. 53–54°/60 mm. (Found: C, 41.0; H, 4.9; Br, 54.0. $\text{C}_6\text{H}_9\text{Br}$ requires C, 40.8; H, 4.8; Br, 54.4%); $\nu_{\text{max.}}$ 1950vs ($\text{C}=\text{C}$), 1160vs, 1050vs, 750vs, and 730 cm^{-1} ; g.l.c. (dinonyl phthalate; 82°) showed one main peak, t , 6½ min.

(b) A mixture of 3-methylbut-1-yn-3-ol (90.7 g., 1.08 mole) cuprous bromide (43 g., 0.3 mole), ammonium bromide (32.4 g.), copper powder (2 g.), and concentrated hydrobromic acid (48% w/w, 216 ml., 1.91 mole) was shaken in a closed flask at room temperature for 23 hr. and then worked up, as above. Fractionation gave 1-bromo-3-methylbuta-1,2-diene (112.5 g., 71%), b. p. 58.5–60°/60 mm.

1-Bromo-3-methylpenta-1,2-diene.—(a) 3-Methylpent-1-yn-3-ol (14.7 g., 0.15 mole) was added over 6 min. to a vigorously stirred mixture of cuprous bromide (7.5 g., 0.052 mole), ammonium bromide (6 g.), copper powder (0.3 g.), and hydrobromic acid (48% w/w, 36 ml., 0.32 mole) at 40°, and stirring was continued for a further 45 min. Working up gave 1-bromo-3-methylpenta-1,2-diene (17 g., 73%), b. p. 51–52.5°/24 mm. (Found: C, 44.4; H, 5.6; Br, 49.6. $\text{C}_8\text{H}_{11}\text{Br}$ requires C, 44.75; H, 5.6; Br, 49.65%); $\nu_{\text{max.}}$ 1950vs ($\text{C}=\text{C}$), 1165vs, and 730vs cm^{-1} ; $\lambda_{\text{max.}}$ 201 $\text{m}\mu$ (ϵ 7100), $\lambda_{\text{sh.}}$ 217–223 $\text{m}\mu$ (ϵ 6150); g.l.c. (dinonyl phthalate; 82°) showed only one peak, t , 12.5 min.; n.m.r. showed a quartet of doublets $\tau = 8.19$ ($\text{CH}=\text{C}-\text{CMe}-\text{CH}_2-\text{Me}$), $J_{5,4} = 7.5$ c./sec., a 1 : 5 : 10 : 10 : 5 : 1 sextet $\tau = 4.1$ ($\text{CH}=\text{C}-\text{CMeEt}$), $J_{4,1} = 2.3$ c./sec. (double resonance of the C_6H_5 group causes collapse of the sextet to a triplet), a triplet at $\tau = 8.93$ ($\text{CH}=\text{C}-\text{CMe}-\text{CH}_2-\text{Me}$), $J_{5,4} = 7.5$ c./sec., a doublet of triplets $\tau = 7.6$ – 8.4 ($\text{CH}=\text{C}-\text{CMe}-\text{CH}_2-\text{Me}$), $J_{6,1} = 2$ c./sec., and $J_{6,4} = 0.5$ c./sec.

(b) 3-Methylpent-1-yn-3-ol (98 g., 1 mole), cuprous bromide (50 g., 0.35 mole), ammonium bromide (40 g., 0.41 mole), copper powder (2 g.), and hydrobromic acid (48% w/w, 240 ml., 2.1 mole), was stirred at room temperature for 45 min. and then warmed to 40° and stirred for a further 45 min. Working up gave the product (140 g., 87%), b. p. 58–60°/35 mm.

1-Bromo-3-ethylpenta-1,2-diene.— 3-Ethylpent-1-yn-3-ol (56.0 g., 0.5 mole), cuprous bromide (28.9 g., 0.2 mole), ammonium bromide (20.0 g., 0.2 mole), copper powder (2.8 g.), and hydrobromic acid (45% w/w, 124 ml., 1.0 mole), treated at 40° for 1½ hr. gave 1-bromo-3-ethylpenta-1,2-diene (56.9 g., 65%), b. p. 74°/30 mm. (Found: C, 47.8; H, 6.2; Br, 45.9. $\text{C}_7\text{H}_{11}\text{Br}$ requires C, 48.0; H, 6.3; Br, 45.7%);

⁶ Unpublished work by B. Dimitriou and S. R. Landor.

⁷ E. I. Snyder and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 1582.

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n_D^{24} 1.5015; ν_{\max} 1950vs (C=C=C), 720 cm^{-1} ; λ_{\max} 206 μ (ϵ 7800), λ_{sh} 220 μ (ϵ 7100); g.l.c. (silicone oil; 151°), t , 9½ min.; n.m.r. showed a 1:4:6:4:1 quintet $\tau = 4.0$ ($\text{CH}=\text{C}=\text{C}(\text{Et})\text{CH}_2-\text{Me}$), $J_{1,4} = 2.2$ c./sec., a quartet of doublets $\tau = 7.85$ ($\text{CH}=\text{C}=\text{C}(\text{Et})\text{CH}_2-\text{Me}$), $J_{4,1} = 2.2$ c./sec., $J_{5,4} = 7.8$ c./sec., and a triplet at $\tau = 8.94$ ($\text{CH}=\text{C}=\text{C}(\text{Et})\text{CH}_2\text{Me}$), $J_{4,5} = 7.5$ c./sec.

Similarly, with 60% hydrobromic acid for 25 min., a 77% yield of bromoallene was obtained which, however, contained 10% of bromoacetylene.

1-Bromo-3,4,4-trimethylpenta-1,2-diene.—(a) 3,4,4-Trimethylpent-1-yn-3-ol (63 g., 0.5 mole), cuprous bromide (85 g., 0.59 mole), ammonium bromide (42 g.), copper powder (6 g.), and hydrobromic acid (48% w/w, 180 ml., 1.6 mole), warmed to 40° and stirred for 2 hr., gave 1-bromo-3,4,4-trimethylpenta-1,2-diene (73.2 g., 78%), b. p. 45—47°/5 mm. (Found: C, 50.5; H, 7.1; Br, 42.3. $\text{C}_8\text{H}_{13}\text{Br}$ requires C, 50.8; H, 6.95; Br, 42.25%); ν_{\max} 1950vs (C=C=C), 1155vs, and 728vs cm^{-1} ; λ_{\max} 201 μ (ϵ 9000), 224 μ (ϵ 6600); n.m.r. showed a doublet $\tau = 8.21$ ($\text{CH}=\text{C}=\text{CMeBu}^t$), and a quartet $\tau = 4.17$ ($\text{CH}=\text{C}=\text{CMe}$), $J_{4,1} = 2.0$ c./sec.; g.l.c. (dinonyl phthalate; 100°), t , 20 min.

(b) 3,4,4-Trimethylpent-1-yn-3-ol (19.9 g., 0.15 mole), ammonium bromide (9 g.), copper powder (1.5 g.), and concentrated hydrobromic acid (48% w/w, 36 ml., 0.32 mole) was shaken for 36 hr. at room temperature and worked up to give the product (23 g., 81%), b. p. 57—61°/10 mm.

1-Bromo-3-isopropyl-4-methylpenta-1,2-diene.—(a) 3-Isopropyl-4-methylpent-1-yn-3-ol (56 g., 0.4 mole), cuprous bromide (68 g., 0.47 mole), ammonium bromide (36 g.), copper (6 g.), and hydrobromic acid (48% w/w, 144 ml., 1.27 mole) treated at 40° for 3 hr. gave 1-bromo-3-isopropyl-4-methylpenta-1,2-diene (66.2 g., 82%), b. p. 49—50°/6 mm. (Found: C, 53.6; H, 7.1; Br, 39.7. $\text{C}_9\text{H}_{15}\text{Br}$ requires C, 53.2; H, 7.45; Br, 39.3%); ν_{\max} 1950s (C=C=C), 1660vw (C=C), 1165s, and 895w cm^{-1} ($\text{CR}_1\text{R}_2=\text{CH}_2$); λ_{\max} 201 μ (ϵ 9750) λ_{sh} , 219—223 μ (ϵ 6850); g.l.c. (dinonyl phthalate; 100°) showed only one peak, t , 20 min.

(b) 3-Isopropyl-4-methylpent-1-yn-3-ol (42 g., 0.3 mole), cuprous bromide (40 g., 0.28 mole), ammonium bromide (27 g.), copper powder (3 g.), and hydrobromic acid (60% w/w, 108 ml., 1.36 mole), shaken intermittently for 6 days, gave 1-bromo-3-isopropyl-4-methylpenta-1,2-diene (27.3 g., 45%), b. p. 61—62°/10 mm. The i.r. spectrum was similar to that obtained from the product from (a), except for a stronger band at 895 cm^{-1} due to 1-bromo-3-isopropyl-4-methylpenta-1,4-diene. G.l.c. (silicone oil; 114°) showed one main peak, t , 22 min., with a slight shoulder on its trailing edge, and a small peak (3%), t , 27 min.

1-Bromo-3-isobutyl-5-methylhexa-1,2-diene.—3-Isobutyl-5-methylhex-1-yn-3-ol (51.0 g. 0.3 mole), cuprous bromide (20.0 g., 0.14 mole), ammonium bromide (12.0 g., 0.12 mole), copper powder (2.0 g.), and hydrobromic acid (45%, 72 ml., 0.6 mole) at 40° for 20 hr. gave 1-bromo-3-isobutyl-5-methylhexa-1,2-diene (36.1 g., 52%), b. p. 66°/1.7 mm. (Found: C, 57.2; H, 8.2; Br, 34.6. $\text{C}_{10}\text{H}_{19}\text{Br}$ requires C, 57.1; H, 8.2; Br, 34.6%); ν_{\max} 1965s, 1390m, 1370m, 1165m, 720s cm^{-1} ; λ_{\max} 203 μ (ϵ 9090), 230 μ (ϵ 9000); g.l.c. (G.E.O. 100; 120°), t , 18 min.

1-Bromo-3-*t*-butyl-4,4-dimethylpenta-1,2-diene.—(a) A mixture of 3-*t*-butyl-4,4-dimethylpent-1-yn-3-ol (16.8 g. 0.1 mole), cuprous bromide (17 g., 0.12 mole), ammonium bromide (9 g.), copper powder (1 g.), and hydrobromic acid (48% w/w, 36 ml., 0.32 mole) when kept for 2 weeks gave 1-bromo-3-*t*-butyl-4,4-dimethylpenta-1,2-diene (18.8 g., 83%),

b. p. 80—81°/6 mm. (Found: C, 57.15; H, 8.2; Br, 35.2. $\text{C}_{11}\text{H}_{19}\text{Br}$ requires C, 57.1; H, 8.3; Br, 34.6%); ν_{\max} 1940ms (C=C=C), 1135s, and 720s cm^{-1} ; λ_{\max} 201 μ (ϵ 12,100), 227 μ (ϵ 7400); n.m.r. showed a singlet, $\tau = 4.16$ ($\text{Bu}^t_2\text{C}=\text{C}=\text{CH Br}$).

(b) 3-*t*-Butyl-4,4-dimethylpent-1-yn-3-ol (25.2 g., 0.15 mole), cuprous bromide (25.5 g., 0.178 mole), ammonium bromide (13.5 g.), copper powder (2 g.), and concentrated hydrobromic acid (48% w/w, 54 ml., 0.48 mole) treated for 17 hr. at 40° gave the product (7.2 g., 21%), b. p. 70—74°/5 mm.

1-Bromo-3-methylocta-1,2-diene.—3-Methyloct-1-yn-3-ol (35.0 g., 0.25 mole), cuprous bromide (12.5 g., 0.09 mole), ammonium bromide (10.0 g., 0.1 mole), copper powder (1.3 g.), and hydrobromic acid (45% w/w, 62 ml., 0.5 mole.) treated for 2½ hr. at 40° gave 1-bromo-3-methylocta-1,2-diene (28 g., 55%), b. p. 68°/1 mm. (Found: C, 52.7; H, 7.3. $\text{C}_9\text{H}_{15}\text{Br}$ requires C, 53.2; H 7.4%); ν_{\max} 1960 (C=C=C) 725s cm^{-1} ; g.l.c. (dinonyl phthalate, 100°), t , 62 min.

Cyclohexylidenevinyl bromide.—Hydrobromic acid (48% w/w, 30 ml., 0.265 mole), cuprous bromide (5 g., 0.035 mole), ammonium bromide (5 g.), copper powder (0.5 g.), and 1-ethynylcyclohexanol (20.6 g., 0.166 mole) were shaken for 45 hr. at room temperature. The upper layer still had ν_{\max} 3500m cm^{-1} (OH). More hydrobromic acid (48% w/w, 10 ml., 0.089 mole), cuprous bromide (2 g.), ammonium bromide (2 g.), and copper powder (1 g.) were added, and after shaking for a further 6 hr. the mixture gave cyclohexylidenevinyl bromide (19.5 g., 63%), b. p. 39—41°/0.3 mm. (Found: C, 51.6; H, 5.8. $\text{C}_8\text{H}_{11}\text{Br}$ requires C, 51.35; H, 5.9%); ν_{\max} 1950m (C=C=C), 1640 and 1580w (C=C), 1150s, and 725s cm^{-1} .

1-Bromobuta-1,2-diene.—A mixture of but-1-yn-3-ol (35 g., 0.5 mole), cuprous bromide (72 g., 0.5 mole), ammonium bromide (45 g.), copper powder (5 g.), and hydrobromic acid (48% w/w, 180 ml., 1.6 mole), was shaken for 4 hr. at room temperature, left overnight, and then shaken for a further 2 hr. Hydrobromic acid (60% w/w, 60 ml., 0.75 mole) was added, and the mixture shaken for 4 hr. Working up gave 1-bromobuta-1,2-diene (27.1 g., 41%), b. p. 62.5—63°/168 mm. (Found: C, 36.4; H, 4.0. $\text{C}_4\text{H}_5\text{Br}$ requires C, 36.1; H, 3.8%); ν_{\max} 3200w (C=CH), 1950s (C=C=C), 1195vs, 840vs, and 680vs cm^{-1} ; g.l.c. (silicone oil; 90°) one main peak, t , 9 min., and one other peak for 3-bromobutene (1—2%), t , 5.5 min.; λ_{\max} 201 μ (ϵ 5200), λ_{inf} 215 μ (ϵ 3500); n.m.r. showed a doublet of doublets at $\tau = 8.22$ ($\text{MeCH}=\text{C}=\text{CH}$), $J_{4,1} = 2.6$ c./sec., a doublet of quartets at $\tau = 4.09$ ($\text{Me CH}=\text{C}=\text{CH}$), $J_{3,1} = 5.8$ c./sec., and a doublet of quartets at $\tau = 4.68$ ($\text{MeCH}=\text{C}=\text{CH}$), $J_{4,1} = 6.9$ c./sec.

1-Bromopenta-1,2-diene.—Pent-1-yn-3-ol (21 g., 0.25 mole), cuprous bromide (36 g., 0.25 mole), ammonium bromide (24.5 g., 0.25 mole), copper powder (4 g.), and hydrobromic acid (60% w/w, 96 ml., 1.24 mole) left at room temperature for 9 hr. gave 1-bromopenta-1,2-diene (20.5 g., 56%), b. p. 62°/66 mm. (Found: C, 41.0; H, 5.1; Br, 53.1. $\text{C}_5\text{H}_7\text{Br}$ requires C, 40.85; H, 4.8; Br, 54.4%). ν_{\max} 1950s (C=C=C), 1190vs, 850vs, and 690vs cm^{-1} ; λ_{\max} 205 μ (ϵ 7000), λ_{inf} 215 μ (ϵ 5500); g.l.c. (silicone oil; 104°) showed one main peak (99%), t , 5 min., and a small peak at t , 2½ min. (<1%, 3-bromopentyne).

1-Bromohexa-1,2-diene.—Hex-1-yn-3-ol (49 g., 0.5 mole), cuprous bromide (67 g., 0.47 mole), ammonium bromide (45 g.), copper powder (5 g.), and hydrobromic acid (60% w/w, 180 ml., 2.3 mole), set aside at room temperature for

10 hr., left overnight, and then shaken for a further 3 hr., gave 1-bromohexa-1,2-diene (53.5 g., 67%), b. p. 51.5—52.5°/22 mm. (Found: C, 45.5; H, 5.9; Br, 49.1. C_6H_9Br requires C, 44.75; H, 5.6; Br, 49.6%); ν_{max} 1950s (C=C=C), 1190vs, 830, and 690 cm^{-1} ; λ_{max} 202 $m\mu$ (ϵ 7200), λ_{inf} 215 $m\mu$ (ϵ 4700).

1-Bromo-4-methylpenta-1,2-diene.—(a) 4-Methylpent-1-yn-3-ol (19.6 g., 0.2 mole), cuprous bromide (27 g., 0.19 mole), ammonium bromide (18 g.), copper powder (2 g.), and hydrobromic acid (60% w/w, 72 ml., 0.91 mole), shaken at room temperature for 23 hr., gave 1-bromo-4-methylpenta-1,2-diene (9.9 g., 31%), b. p. 60—62°/35 mm. (Found: C 45.0; H, 5.6; Br, 49.3. C_6H_9Br requires C, 44.7; H, 5.6; Br, 49.6%). All the fractions had ν_{max} 3250w (C≡CH), 1950s (C=C=C), 1195s, 855s, and 704s cm^{-1} ; g.l.c. (silicone oil; 100°) showed two peaks, t , 8 min. (95%) and t , 10 min. (5%, 3-bromohex-1-yne).

(b) As for (a) except that 48% hydrobromic acid was used, at room temperature for 6 days, and then hydrobromic acid (48% w/w, 30 ml., 0.26 mole) was added; the mixture was shaken for a further day, and worked up to give

1-bromo-3-methylpenta-1,2-diene (7.3 g., 23%), b. p. 55—56°/34 mm.; ν_{max} 1950s (C=C=C), 1195s, 855s, and 704s cm^{-1} ; there was no band at 3300 cm^{-1} (C≡CH).

(c) 4-Methylpent-1-yn-3-ol (39.2 g., 0.4 mole), cuprous bromide (58 g., 0.4 mole), ammonium bromide (40 g., 0.4 mole), copper powder (4 g.), and hydrobromic acid (45% w/w, 248 ml., 2 mole) was shaken at room temperature for 42 hr. Hydrobromic acid (60% w/w, 25 ml., 0.35 mole) was then added and the mixture shaken for a further 4 hr., giving 1-bromo-4-methylpenta-1,2-diene (23 g., 35%), b. p. 60—62°/35 mm.; ν_{max} 1950s (C=C=C), 1195s, 855s, and 704s cm^{-1} with no band at 3300 cm^{-1} (C≡CH); g.l.c. (dinonyl phthalate; 120°) gave one peak, t , 5½ min.

We thank Dr. Mooney and Dr. White for n.m.r. data, the Chemical Society for a grant from the Research Fund, Parke-Davis Limited for a Fellowship (to P. F. W.), and the S.R.C. and N.A.T.O. for a studentship (to P. M. G.).

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LONDON S.E.18. [6/096 Received, January 24th, 1966]